

The Effect of Curing Conditions on the Properties of Geopolymer Samples

E. Arioiz, Ö. Arioiz, and Ö. M. Koçkar

Abstract—Geopolymers or inorganic polymers are getting increasing attention due to being environmentally friendly and having great potential for applications in various industries. Geopolymers have three dimensional amorphous structure and can be synthesized from by products such as fly ash, blast furnace slag or geological materials such as kaolinite.

In this experimental study F class fly ash was used as a raw material and geopolymer samples were synthesized by means of sodium silicate and 8 M sodium hydroxide solutions. These samples were cured at 80 °C for three different durations (6h, 15h and 24h). Compressive strength tests were carried out at 7 and 28 days. The maximum compressive strength was found to be 40.35 MPa. The compressive strength values indicated that the curing conditions influenced the physical properties of geopolymer samples. As the curing duration increased, the compressive strengths increased.

XRD and FTIR techniques were used to characterize the fly-ash based geopolymers. In FTIR spectra it has been seen that geopolymerisation has been achieved successfully. The major fingerprint for the geopolymer has been obtained. It was also observed that there was no significant effect of curing conditions on the microstructure of the samples. FTIR and XRD spectrums were nearly the same with increasing duration.

Index Terms—Geopolymer, mechanical properties, characterization.

I. INTRODUCTION

As the “greenhouse” gases have rising levels in the atmosphere, and the temperature of the environment increases, present life forms of the planet alters. The most important greenhouse gas is carbon dioxide. The cement production industry has been identified as one of the most important users of carbon-based fuels [1]. Cement production generates 5–8% of the world’s CO₂ emissions. In the coming decades the emissions increase dramatically as CO₂ savings are found in other industries, while the cement industry will be constrained by the dual issues of rising demand and the limitations on CO₂ efficiency due to the fundamental chemistry [2].

For the solution of some problems inorganic polymer cements have been proposed. As they provide the potential for very significant (on the order of 80%) CO₂ savings while offering at least comparable performance in many areas [2]. Inorganic polymers or “geopolymers” are three dimensional

aluminosilicate materials and have ceramic- like properties [3].

The reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide and/or silicate solution produces a synthetic alkali aluminosilicate material generally called a “geopolymer”, but more broadly termed an ‘inorganic polymer’ [4].

They are amorphous to crystalline reaction products from synthesis of alkali aluminosilicates from reaction with alkali hydroxide/alkali silicate solution [4]. Polymerization occurs under highly alkaline conditions, when reactive aluminosilicate materials are rapidly dissolved and free [SiO₄] and [AlO₄] tetrahedral units are released into solution. During the reaction, water is gradually split out and tetrahedral units are alternatively linked to polymeric precursors by sharing oxygen atoms between two tetrahedral units and thereby forming amorphous geopolymers [3].

The exact reaction mechanism of geopolymers is not fully understood. Most proposed mechanisms consist of a dissolution, transportation or orientation, as well as a reprecipitation (polycondensation) step [5].

Many materials containing large amounts of silica and alumina that partially dissolve in alkaline solutions have been used as reagents for geopolymerisation reactions. These include natural minerals (kaolinite, feldspar, albite, stilbite), treated minerals (metakaolinite) and waste materials [6]. Most waste materials such as fly ash, blast furnace slag and mine tailings contain sufficient amounts of reactive alumina and silica that can be used as source materials for geopolymerisation reactions [7].

Depending on the composition of starting materials, the binders can be divided into two groups: (a) alkaline-earth alkali binding system and (b) alkaline binding system. Alkali-activated blast furnace slag cement is a typical example for the first group and alkali-activated metakaolin or fly ash cement for the second group [8], [9]. The kind of reaction product and their proportion should mainly influence special properties e.g. acid resistance, and might also influence the hardening behaviour [10].

Depending on the raw material selection and processing conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance, low thermal conductivity adhesion to fresh and old concrete substrates, steel, glass, ceramics. But not all the geopolymer products will have all of these properties. According to the desired property and the applications of the geopolymers, they can be synthesized with different formulations at a minimum cost [4]-[11].

Geopolymers can be synthesized by mixing

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aluminosilicate source with both strong alkali solutions like sodium hydroxide or potassium hydroxide and silicate solutions like sodium silicate or potassium silicate. In geopolymerisation, it was found that NaOH plays an important role on the compressive strength and the structure of products. Also, the concentration of the alkali solution affects the dissolution mechanism [12]. The curing conditions, both curing duration and curing temperature, are another important factors affecting the mechanical properties and the microstructure of geopolymers.

II. EXPERIMENTAL STUDY

In this study F class fly ash, sodium hydroxide and sodium silicate were used for geopolymerisation and the pastes were cured at different conditions. Mechanical properties were investigated by compressive strength tests. X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy techniques were used for the microstructure analysis.

F class fly ash used in the synthesis was obtained from Çatalagzi thermal power plant. Technical sodium hydroxide and sodium silicate solutions were used for alkali activation. 8 M NaOH solution was prepared before at least 24 hours before the synthesis to cool down to room temperature. Sodium silicate was added to sufficient amount of sodium hydroxide with continuous stirring and then the mixture was added to fly ash. Then the prepared paste was stirred to obtain homogeneous mixture. The paste was cast into 4x4x16 cm steel molds and vibrated to avoid the air bubbles.

The specimens were cured at 80 °C for 6 h, 15 h and 24 h. De-molded geopolymer pastes kept at room temperature for 7, 28 and 90 days aging. The compressive strength tests were carried out for all specimens.

After 28 days aging, microstructures of geopolymers were investigated by FTIR spectroscopy and XRD techniques.

III. RESULTS

The compressive strength values of the 7 days aged geopolymer samples are given in Table I.

TABLE I: THE COMPRESSIVE STRENGTH VALUES OF GEOPOLYMER SAMPLES AGED FOR 7 DAYS

Curing Duration (hour)	Compressive Strength (MPa)
6	8,78
15	23,25
24	28,6

The minimum compressive strength was found as 8, 78 MPa for 7 days aged samples. The compressive strength were 23, 25 MPa and 28, 6 MPa for 15 hours and for 24 hours respectively. The compressive strengths increased with curing duration as can be seen graphically in Fig. 1.

As seen in the Fig. the compressive strength increased sharply when the duration increased to 15 hours from 6 hours. The compressive strengths for the 28 days aged geopolymer samples are given in Table II.

The compressive strengths were slightly increased with

curing duration after 28 days aging. The maximum compressive strength was 33,18 MPa at 24 hours. Fig. 2 shows that the compressive strength of the samples aged for 28 days.

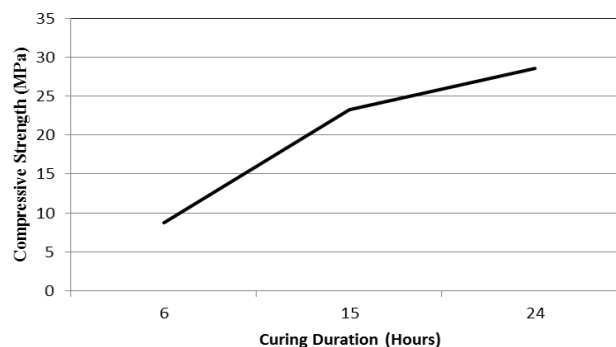


Fig. 1. Compressive strength values of geopolymer samples after 7 days.

TABLE II: THE COMPRESSIVE STRENGTH VALUES OF GEOPOLYMER SAMPLES AGED FOR 28 DAYS

Curing Duration (hour)	Compressive Strength (MPa)
6	22,55
15	29,85
24	33,18

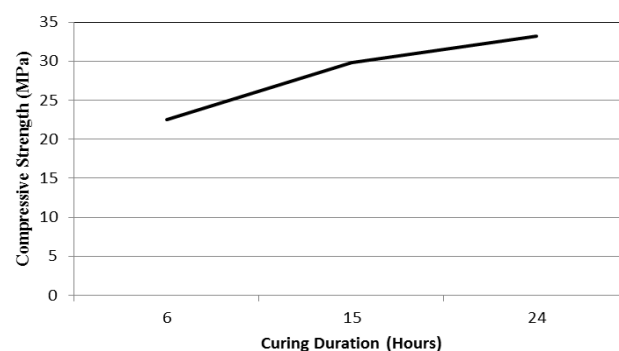


Fig. 2. Compressive strength values of geopolymer samples after 28 days.

The compressive strength of the samples increased with duration but the increment was not sharp as the strengths for 7 days aging. The increment of the strength is 0, 3% for 28 days aging while 1, 6% for 7 days aging whenever the duration increased to 15 hours.

In Table III, the strengths of the specimens after 90 days aging are given.

TABLE III: THE COMPRESSIVE STRENGTH VALUES OF GEOPOLYMER SAMPLES AGED FOR 90 DAYS

Curing Duration (hour)	Compressive Strength (MPa)
6	35,8
15	35,39
24	40,69

After 90 days aging, the compressive strength of the sample cured for 15 hours decreased slightly. As the duration increased, the strength again increased and reached to 40, 69 MPa. The decrease in the strength can be observed in the Fig. 3.

In Fig. 3, the decrease has seen more evidently. When the curing duration increased to 24 hours the strength increased

sharply and the maximum compressive strength obtained.

The aging of the geopolymer samples affect the compressive strengths as seen above. The effect of aging is pointed out in Fig. 4.

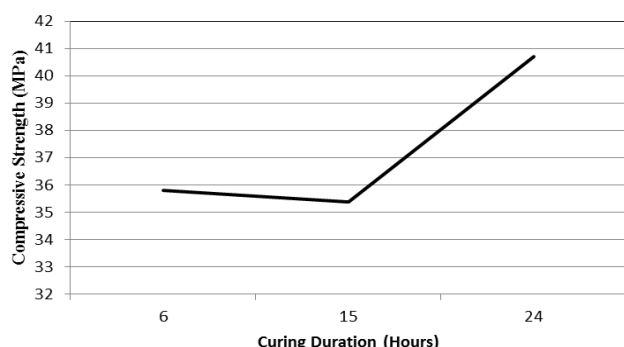


Fig. 3. Compressive strength values of geopolymer samples after 90 days.

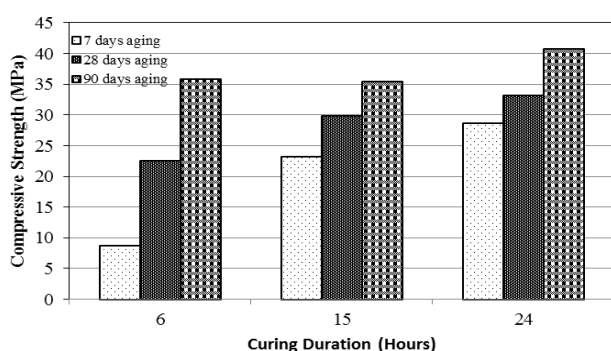


Fig. 4. The effect of aging.

The compressive strengths of all the specimens increased with aging. For 6 hours curing duration, the aging significantly affected the compressive strengths. The strength increased nearly 1, 6 times at 28 days and 59% at 90 days. For 15 hours and 24 hours, the degree of increment was not high as 6 hours. The percentages of increase ranged between 16% and 28%.

The 28 days geopolymer samples were ground to investigate the microstructure of the samples by FTIR spectra and X-ray diffractograms. FTIR spectra of the two samples synthesized at 80 °C and 15 hours and 80 °C and 24 hours are given in Fig. 5 and Fig. 6.

The strong peak at $\sim 1000\text{ cm}^{-1}$ is associated with Al-O and Si-O asymmetric stretching vibrations and is the fingerprint of the geopolymerisation [13]. The bands seen at 3593 cm^{-1} is attributed to stretching vibration of -OH and 1644 cm^{-1} is bending vibrations of H-O-H [14]. Atmospheric carbonation is evident at 1460 cm^{-1} [14]. In the region of $775\text{--}650\text{ cm}^{-1}$, the bands are due to symmetrical vibrations of tetrahedral groups (TO_4). The band at 558 cm^{-1} is correspond to double-ring linkage [15]. The peak at $\sim 460\text{ cm}^{-1}$ is assigned to in-plane bending of Al-O and Si-O linkages [13].

X-ray diffractograms of the two samples are given in Fig. 7 and Fig. 8.

It was observed that geopolymer samples have amorphous phases and crystalline phases consists of quartz and mullite crystals.

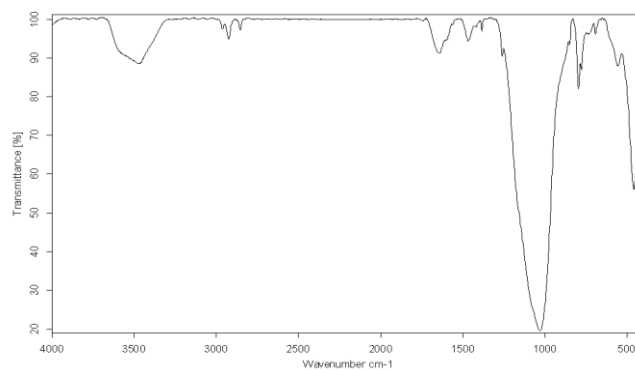


Fig. 5. FTIR spectrum of geopolymer sample cured at 80 °C for 15 hours.

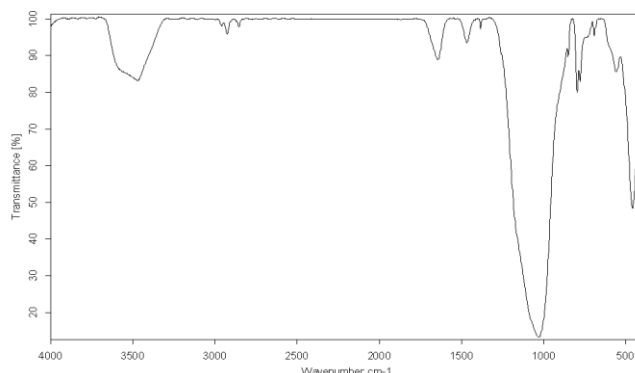


Fig. 6. FTIR spectrum of geopolymer sample cured at 80 °C for 24 hours.

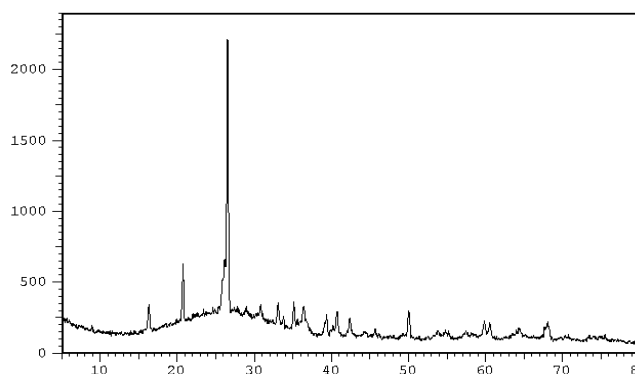


Fig. 7. XRD pattern of the geopolymer sample cured at 80 °C for 15 hours.

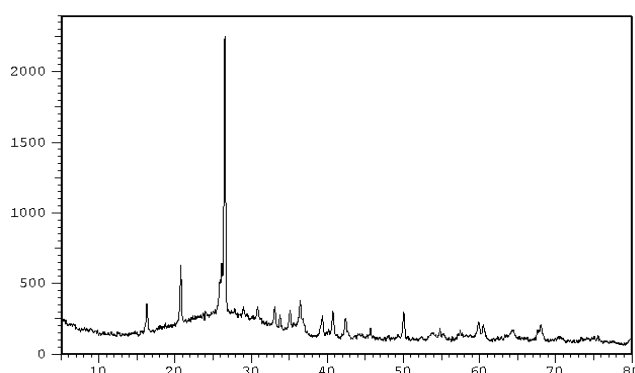


Fig. 8. XRD pattern of the geopolymer sample cured at 80 °C for 24 hours.

IV. DISCUSSIONS

The results showed that the compressive strength of the samples increased with increase in curing duration but only the compressive strength of the geopolymer cured for 15 hours and aged after 90 days was lower than the 6 hours cured sample.

The compressive strengths increased with aging. The

effects of aging on the compressive strength was found to be more significant for short curing times such as 6 hours.

In FTIR spectra, Al-O and Si-O asymmetric stretching vibrations which is the fingerprint of the geopolymerisation increased with duration.

XRD diffractograms indicated that crystalline parts of the geopolymer samples was not changed significantly by curing duration.

V. CONCLUSIONS

Geopolymers are new materials which have various application fields. There are many parameters affecting the geopolymerisation. In this experimental study, the curing conditions on the final properties of fly-ash based geopolymers were investigated.

The compressive strength values indicated that the curing conditions influenced the physical properties of geopolymer samples. As the curing duration increased, the compressive strengths increased. The decrease in the sample cured for 15 hours after 90 days aging can be based on its brittle structure [16]-[17].

In FTIR spectra it has been seen that geopolymerisation has been achieved successfully. The major fingerprint for the geopolymer has obtained. The bond structure of the samples cured 80 °C for 15 hours and 24 hours were the same, the intensities differed only a few.

It was also observed that there was no significant effect of curing conditions on the microstructure of the samples. FTIR and XRD spectrums were nearly the same with increasing duration.

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